(12) UK Patent Application (19) GB (11) 2 144 133 A

(43) Application published 27 Feb 1985

(21) Application No 8418960

(22) Date of filing 25 Jul 1984

(30) Priority data
(31) 8312257 (32) 25 Jul 1983 (33) FR

(51) INT CL³
C08L 33/00 A61K 7/06 7/48 C08L 29/06

(52) Domestic classification
C3P 150 156 210 220 222 274 302 304 316 322 328 662 FE FF
A5B 161 FC FH
U1S 1343 C3P

(56) Documents cited
US A 3884964

(58) Field of search
C3P
C3V
A5B

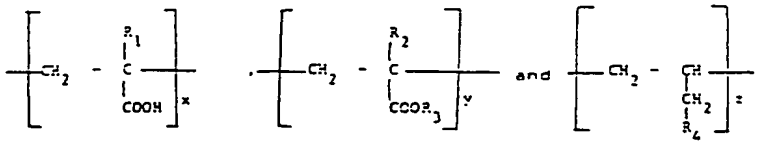
(71) Applicant
L'Oreal (France),
14 rue Royale, 75008 Paris, France

(72) Inventors
Claude Mahieu
Christos Papantoniou

(74) Agent and/or Address for Service
J A Kemp & Co,
14 South Square, Gray's Inn, London WC1R 5EU

# (54) Cosmetic compositions for the hair and the skin containing a copolymer of (meth)acrylic acid, an alkyl (meth)acrylate and an allyl derivative

(57) Cosmetic compositions particularly suitable for application to the hair or skin contain, in a suitable vehicle, at least one acrylic copolymer having repeat units corresponding to the following formulæ:



(1a) (1b) (1c)

in which:
$R_1$ and $R_2$ represent H or $CH_3$,
$R_3$ represents a $C_1$–$C_{10}$ alkyl radical,
and $R_4$ represents –OH, $-NHCONH_2$ or $-OCOR_5$, with $R_5$ representing a $C_1$–$C_5$ alkyl radical, and with
x representing 40 to 90%
y 8 to 50%,
z 2 to 25% and
x + y + z 80 to 100% by weight of the copolymer units.

GB 2 144 133 A

SPECIFICATION

**Cosmetic compositions for the hair and the skin containing a copolymer of acrylic or methacrylic acid, and alkyl acrylate and/or methacrylate and an allyl derivative**

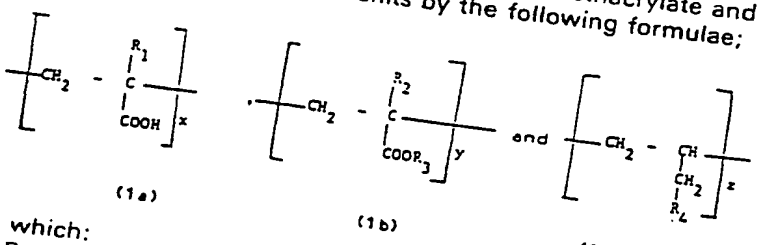
The present invention relates to cosmetic compositions based on a copolymer of acrylic or methacrylic acid, and alkyl acrylate and/or methacrylate and an allyl derivative, in particular compositions for the hair and the skin. Such polymers make it possible to impart properties which are particularly desired in cosmetics.

The compositions for hair make it possible to impart more bulk and better style retention without the appearance of cosmetically unattractive phenomena such as dusting, sticking or a stiff appearance of the hair.

Moreover, the compositions facilitate the combing-out of the hair and increase the gloss of the hair.

When these polymers are present in compositions for the skin, they impart a smoother appearance to the skin and make it softer to the touch, and also improve the texture of the compositions.

The present invention provides a cosmetic composition which contains, in a suitable cosmetic vehicle, at least one copolymer consisting essentially of repeat units derived from acrylic or m thacrylic acid, and alkyl acrylate and/or methacrylate and an alkyl derivative it being possible to represent the said repeat units by the following formulae;



(1a) (1b) (1c)

which:

$R_1$ and $R_2$ represent a hydrogen atom or a methyl radical,

$R_3$ represents a linear or branched alkyl radical having from 1 to 10 carbon atoms,

$R_4$ represents $-OH$, $-NHCONH_2$ or $-OCOR_5$, with $R_5$ representing a linear or branched alkyl ical having from 1 to 5 carbon atoms.

x representing from 40 to 90% by weight,

y representing from 8 to 50% by weight and

z representing from 2 to 25% by weight, with $x + y + z$ being from 80 to 100%.

The copolymers of the compositions according to the invention, as defined above, suitably have a weight-average molecular weight of 5,000 to 200,000, and preferably 10,000 to 00, measured according to the light diffusion method.

The repeat units of the formula (1a) are derived from acrylic acid or methacrylic acid.

The repeat units of the formula (1b) are derived from a lower alkyl acrylate and/or crylate, especially methyl, ethyl, propyl, isopropyl, butyl, hexyl, 2-ethylhexyl or octyl or m thacrylate.

The repeat units of the formula (1c) are derived from, for example allyl alcohol, allyl acetate, pionate or allyl-urea.

According to a preferred embodiment, the copolymers are those in which:

the repeat units of the formula (1a) represent from 50 to 85% by weight,

the repeat units of the formula (1b) represent from 10 to 35% by weight and

the sum $x + y + z$ as defined above is less than 100% the remainder consists of repeat unspecified structure.

Among the copolymers of the compositions according to the invention, there may be mentioned those containing repeat units derived from the polymerisation of:

acrylic acid, methyl acrylate and allyl alcohol,

methacrylic acid, methyl methacrylate and allyl alcohol,

acrylic acid, methyl acrylate, methyl methacrylate and allyl alcohol,

methacrylic acid, methyl methacrylate and allyl alcohol,

acrylic acid, methyl acrylate and allyl alcohol,

methacrylic acid, ethyl acrylate and allyl alcohol,

acrylic acid, ethyl methacrylate and allyl alcohol,

methacrylic acid, isopropyl acrylate and allyl alcohol,

methacrylic acid, ethyl

solar radiation filters, fillers, stabilisers and softeners.

These compositions make it possible to impart to the skin a pleasant softness to the touch, and make the skin smooth.

These compositions constitute, in particular, treatment creams or lotions for the hands or face, sunbathing creams, tinted creams, make-up remover milks, bath foam liquids, after-shave lotions, toilet waters, shaving foams, rouge pencils, coloured or colourless lipsticks, make-up sticks or body hygiene sticks, or deodorant compositions.

The copolymers defined above can be present in the skin treatment compositions either as an additive or as the main active ingredient.

These compositions for the skin can moreover contain various active substances such as moisturising agents, cicatrising agents and anti-inflammatory agents and can be in the form of, for example, aqueous or aqueous-alcoholic solutions, creams, or milks.

The copolymers, some of which are described in U.S. Patent 3,884,964 can be obtained in accordance with conventional polymerisation methods, that is to say polymerisation in solution in a solvent, mass polymerisation or, optionally, emulsion polymerisation.

The solution polymerisation process is generally carried out in an inert solvent, such as ethyl acetate.

The polymerisation initiators which can be used in this polymerisation process are preferably azo-bis-isobutyronitrile, per-esters, per-carbonates or oxidation-reduction systems. The polymerisation initiator can be used either as an individual substance or as a mixture.

The amount of polymerisation initiator is generally 0.1 to 6% by weight relative to the total weight of the monomers to be copolymerised.

The polymerisation reaction is preferably carried out at a temperature of 45 to 100°C and more especially at the reflux temperature of the reaction mixture.

The reaction time is preferably 2 to 24 hours.

Another particularly advantageous process can be used where it is desired to obtain polymers in which the radicals $R_1$ and $R_2$ are identical, that is to say represent either a hydrogen atom or a methyl radical.

In fact, in this particular case the polymerisation reaction can be carried out in solution in an alcohol capable of partially esterifying the carboxylic acid groups of the acrylic or methacrylic acid starting material.

This process is very particularly preferred where the radical $R_3$ of the repeat units of the formula (1b) represents an alkyl radical having from 1 to 3 carbon atoms.

According to this method, the polymerisation reaction is carried out starting from acrylic or methacrylic acid and at least one monomer capable of producing repeat units of the formyla (1c).

During the polymerisation reaction, partial esterification of the acid groups of the acrylic or methacrylic acid by the lower aliphatic alcohol used as the solvent takes place.

According to this process, it is thus possible to esterify up to about 20% of the acid groups of the acrylic or methacrylic acid starting materials.

In this process, the polymerisation initiators can be those usually employed, such as organic compounds of the peroxide, per-ester or per-carbonate type, but preferably azo-bis-isobutyronitrile or oxidation-reduction systems.

By varying certain parameters of the working conditions it is possible to control the molecular weight of the copolymers which it is desired to obtain. In general, these parameters, are, on the one hand, the amount of polymerisation initiator and, on the other hand, the monomer concentration in the reaction solvent.

According to a preferred embodiment, where it is desired to obtain polymers of molecular weight 10,000 to 50,000, the process consists of copolymerising acrylic acid or methacrylic acid and the monomer leading to repeat units of the formula (1c) in solution in an aliphatic alcohol capable of partially esterifying the repeat units of the formula (1a), in the presence of hydrogen peroxide and of a reagent which accelerates the formation of free radicals. This accelerating reagent can be ultra-violet irradiation or an inorganic or organic compound possessing reducing properties. Amongst the latter compounds there may in particular be mentioned ferrous chloride, cuprous chloride, and ascorbic acid.

If it is desired to achieve a higher degree of esterification of the repeat units of the formula (1a), the copolymerisation reaction should be carried out in the presence of a strong acid such as sulphuric acid or para-toluenesulphonic acid.

The following Examples further illustrate the present invention and the preparation of the copolymers used therein.

*EXAMPLE 1:* Preparation of a polymer containing 68% of acrylic acid/8% of ethyl acrylate/12% of allyl alcohol (the remainder consisting or repeat units of indeterminate structures).

320 g of acrylic acid, 800 ml of ethanol, 80 g of allyl alcohol and 60 g of a 30% strength hydrog n peroxide solution are introduced into a 2 litre reactor equipped with a stirrer, a

condenser, a nitrogen inlet and a tube for the introduction of the reactants.

The mixture is then heated to 80°C. When the temperature has been reached, heating is stopped and the dispersion of 400 mg of cuprous chloride in 400 ml of water is introduced. From the time of addition of the first drops of the dispersion, the temperature of the reaction mixture rises to 83°C, and vigorous reflux of ethanol is therefore observed. The addition of the dispersion is then regulated so that it is completed in 40 minutes, the mixture being heated if necessary in order to maintain the refluxing of the solvent.

The polymerisation reaction is then continued at the reflux temperature of the solvent for about 2 hours 30 minutes.

After it has cooled, the reaction mixture is concentrated to half on a rotary evaporator and is then poured into trays and dried in an oven at 50°C under $26.10^2$Pa.

Analyses:

Acid number: 532

Viscosity of a 50% strength solution of the polymer in water at 25°C: 217 cPo.

The ester and alcohol contents are determined by proton NMR.

*EXAMPLE 2:* Preparation of a polymer containing 64% of acrylic acid/8% of ethyl acrylate/12% of allyl alcohol (the remainder consisting of repeat units of indeterminate structures).

320 g of acrylic acid, 800 ml of ethanol, 80 g of allyl alcohol and 60 g of a 30% strength hydrogen peroxide solution are introduced into a 2 litre reactor equipped with a stirrer, a condenser, a nitrogen inlet and a tube for the introduction of the reactants.

The mixture is then brought to a temperature of 80°C. When this temperature has been reached, heating is stopped and a solution of 20 g of ascorbic acid in 40 ml of water is introduced.

As from the addition of the first drops of the solution, the temperature of the reaction mixture rises to 86°C and vigorous refluxing of ethanol is observed. The addition of the solution is then regulated so that it is complete after 40 minutes, the mixture being heated if necessary so as to maintain the refluxing of the solvent. The polymerisation reaction is then continued at the reflux temperature of the solvent for about 2 hours 30 minutes.

After it has cooled, the reaction mixture is diluted with 1500 g of ethyl cellosolve and then concentrated to 1200 g to remove the water, ethanol and residual allyl alcohol completely. The polymer solution is then poured into 15 litres of a 60/40 acetone/petroleum ether mixture, with vigorous stirring. The polymer recovered is then dried at 50°C under $26.10^2$Pa.

Analyses:

Acid number: 497

Viscosity of a 50% strength solution of the polymer in water at 25°C: 740 cPo.

The ester and alcohol contents are determined by proton NMR.

*EXAMPLE 3:* Preparation of a polymer containing 62% of acrylic acid/8% of methyl acrylate/13% of allyl acetate (the remainder consisting of repeat units of indeterminate structures).

297.5 g of acrylic acid, 127.5 g of allyl acetate, 2518 g of methanol and 40 g of 30% strength hydrogen peroxide solution are introduced into a 4 litre reactor equipped with a quartz dip tube containing a Q 2020 UV-emitting lamp, of 2000 W, from the company ORIGINAL HANAU (Federal Republic of Germany). This solution, which is kept stirred under nitrogen, is then irradiated for 2 hours while keeping its temperature at 50°C.

Analysis of the reaction mixture shows that after this time the acrylic acid has been completely consumed.

The reaction mixture is then concentrated to 1000 g, after which it is poured into 20 litres of diethyl ether, with vigorous stirring. The polymer is then dried in an oven at 50°C.

Analyses:

Acid number: 487

Viscosity of a 50% strength aqueous solution at 25°C: 265 cPo.

The methyl ester content was determined by proton NMR.

*EXAMPLE 4:* Preparation of a polymer containing 70% of acrylic acid/9% of methyl acrylate/20% of N-allyl-urea (the remainder consisting of repeat units of indeterminate structures).

160 g of acrylic acid, 40 g of N-allyl-urea, 2240 g of methanol and 40 g of a 30% strength hydrogen p roxide solution are introduced into the same type of reactor as that described in Example 3, and using a process similar to that described there.

The polymerisation reaction is then continued for 4 hours 30 minutes at 50°C, this being the time needed f r complete consumption of th acrylic acid.

The reaction mixture is then concentrated to 1000 g, after which it is poured into 20 litres of diethyl ether, with vigorous stirring. The polymer is then dried in a vacuum oven.

Analysis:

Acid number: 547

Visc sity of a 50% strength aqueous solution at 25°C: 97 cPo.
The methyl ester content was determined by proton NMR.
The N-allyl-urea content was deduced from the percentages of nitrogen found by microanalysis: 5.72%.

*EXAMPLE 5:* Preparation of a polymer containing 67% of acrylic acid/9% of methyl acrylate/12% of allyl alcohol (the remainder consisting of repeat units of indeterminate structures).

340 g of acrylic acid, 85 g of allyl alcohol, 2524 g of methanol and 40 g of a 30% strength hydrogen peroxide solution are introduced into the same type of reactor as that described in Example 3, and using a process similar to that described there.

The polymerisation reaction is then continued for 2 hours at 50°C, this being the time needed for complete consumption of the acrylic acid.

The reaction mixture is then concentrated to 1000 g, after which it is poured into 20 litres of sulphuric ether, with vigorous stirring. The polymer is then dried in an oven at 50°C.

Analysis:
Acid number: 519
Viscosity of a 50% strength aqueous solution at 25°C: 303 cPo.
The methyl ester content was determined by proton NMR.

*EXAMPLE 6:* Preparation of a polymer containing 56% of acrylic acid/17% of ethyl acrylate/11% of allyl alcohol (the remainder consisting of repeat units of indeterminate structures).

160 g of acrylic acid, 40 g of allyl alcohol, 600 g of ethanol and 40 g of azo-bis-isobutyronitrile are introduced into a 3 litre reactor equipped with a nitrogen inlet. The reaction mixture is heated to the reflux temperature of the ethanol for 5 hours. 1 g of azo-bis-isobutyronitrile dissolved in 10 g of ethanol is then added, followed by 100 g of heptane. 300 g of the solvent are then distilled so as to entrain the unpolymerised allyl alcohol.

The reaction mixture then contains less than 2% of residual acrylic acid and the polymer is obtained by pouring the crude solution into 10 litres of diethyl ether, with stirring. The polymer is then dried in an oven at 50°C.

Analyses:
Acid number: 435
Viscosity of a 50% strength solution in water at 25°C: 1670 cPo.
The ethyl ester content was determined by proton NMR.

*EXAMPLE 7:* Preparation of a polymer containing 53% of acrylic acid, 8% of methyl acrylate, 22% of methyl methacrylate and 9% of allyl alcohol (the remainder consisting of repeat units of indeterminate structures).

120 g of acrylic acid, 40 g of methyl methacrylate, 40 g of allyl alcohol, 720 ml of methanol and 30 g of a 30% strength hydrogen peroxide solution are introduced into a 2 litre reactor equipped with a stirrer, a condenser, a nitrogen inlet and a tube for the introduction of the reactants.

The mixture is brought to a temperature of 80°C and then, after having stopped the heating, a solution 10 g of ascorbic acid in water is introduced over 40 minutes. The polymerisation reaction is then continued at the reflux temperature of the solvent for 2 hours 30 minutes. When it has cooled, the mixture is concentrated to 2/3 of its volume on a rotary evaporator and then poured dropwise into 8 litres of acetonitrile, with vigorous stirring. The polymer obtained is then dried in an oven at 50°C.

Analysis:
Acid number: 413
Viscosity of a 50% strength solution in ethanol at 25°C: 1400 cPo.
The ester and alcohol contents are determined by proton NMR (using DMSO as the solvent).

*EXAMPLES OF COMPOSITIONS*

*EXAMPLE A*

A wave-setting lotion is prepared by mixing the following ingredients:

| | |
|---|---|
| polym r prepared according to Example 1. | 2 g |
| sodium hydroxide solution sufficient to giv pH 7 | |
| water sufficient to make up to | 100 g |

In this example, the polymer of Example 1 can be replaced by that of Example 5.

*EXAMPLE B*

A composition in the f rm f a shampo is prepared by mixing the following ingredients:

| | |
|---|---|
| triethanolaminelauryl-sulphate | 10 g |
| polymer prepared according to Example 2 | 1 g |
| sodium hydroxide solution sufficient to give pH 7 | |
| water sufficient to make up to | 100 g |

In this example, the polymer of Example 2 can be replaced by that of Example 6.

*EXAMPLE C*

A composition in the form of shampoo is prepared by mixing the following ingredients:

| | |
|---|---|
| lauryl alcohol polyglycerolated with 4 moles of glycerol | 10 g |
| polymer prepared according to Example 1 | 2 g |
| sodium hydroxide solution sufficient to give pH 7 | |
| water sufficient to make up to | 100 g |

In this example, the polymer of Example 1 can be replaced by that of Example 3.

*EXAMPLE D*

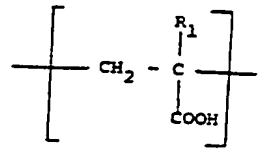
A beauty mask is prepared by mixing the following ingredients:

| | |
|---|---|
| polymer prepared according to Example 2 | 15 g |
| 2-amino-2-methyl-propan-1-ol sufficient to give pH 7 | |
| propylene glycol | 5 g |
| methyl 4-hydroxybenzoate | 0.2 g |
| ethanol | 15 g |
| kaolin | 10 g |
| titanium dioxide | 0.5 g |
| triethanolaminelauryl-sulphate | 0.6 g |
| perfume | 0.15 g |
| sterile demineralised water sufficient to make up to | 100 g |

In this example, the polymer of Example 2 can be replaced by that of Example 4 or of Example 7.

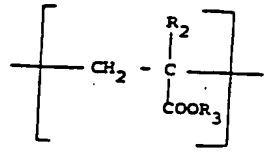
CLAIMS

1. A composition, suitable for use in cosmetics which comprises, in a suitable vehicle, at least one copolymer comprising x repeat units of the formula:



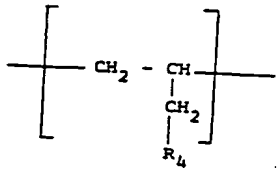
(1a)

y repeat units of the formula



(1b)

and z repeat units of the formula



(1c)

such that:

x represents from 40 to 90% by weight,
y represents from 8 to 50% by weight and
z represents from 2 to 25% by weight with x + y + z + being from 80 to 100% of the copolymer.

in which:

$R_1$ and $R_2$ independently represent a hydrogen atom or a methyl radical,
$R_3$ represents a linear or branched alkyl radical having from 1 to 10 carbon atoms, and
$R_4$ represents $-OH$, $-NHCONH_2$ or $-OCOR_5$, with $R_5$ representing a linear or branched alkyl radical having from 1 to 5 carbon atoms, or a salt thereof.

2. A composition according to claim 1, in which the copolymer has a molecular weight of 5,000 to 200,000 as measured by the light diffusion method.

3. A composition according to claim 2 in which the copolymer has a molecular weight of 10,000 to 50,000.

4. A composition according to any one of the preceding claims, in which the repeat units of formula (1b) of the copolymer are derived from methyl, ethyl, propyl, isopropyl, butyl, hexyl, 2-ethylhexyl or octyl acrylate or methacrylate.

5. A composition according to any one of claims 1 to 4 in which the repeat units of formula (1c) of the copolymer are derived from allyl alcohol, allyl acetate, allyl propionate or allyl-urea.

6. A composition according to any one of the preceding claims, in which, in the copolymer, the repeat units of formula (1a) represent from 50 to 85% by weight, the repeat units of formula (1b) represent from 10 to 35% by weight and the repeat units of formula (1c) represent from 5 to 15% by weight.

7. A composition according to any one of the preceding claims, in which the copolymer consists of repeat units derived from either:

–acrylic acid, methyl acrylate and allyl alcohol,
–acrylic acid, methyl methacrylate and allyl alcohol,
–acrylic acid, methyl acrylate, methyl methacrylate and allyl alcohol,
–methacrylic acid, methyl methacrylate and allyl alcohol,
–methacrylic acid, methyl acrylate and allyl alcohol,
–acrylic acid, ethyl acrylate and allyl alcohol,
–methacrylic acid, ethyl methacrylate and allyl alcohol,
–acrylic acid, isopropyl acrylate and allyl alcohol,
–methacrylic acid, ethyl methacrylate and allyl acetate or
–acrylic acid, ethyl acrylate and allyl-urea.

8. A composition according to any one of the preceding claims, in which the acid groups of the copolymer are neutralised completely or partially with an inorganic or organic base.

9. A composition according to claim 8, in which the organic base is monoethanolamine, diethanolamine, triethanolamine, isopropanolamine, morpholine, 2-amino-2-methylpropan-1-ol or 2-amino-2-methyl-propane-1,3-diol

10. A composition according to any one of the preceeding which contains the copolymer at a concentration of 0.1 to 30% by weight.

11. A composition according to claim 10 to which contains the copolymer at a concentration of 0.5 to 10% by weight.

12. A composition according to any one of the preceeding claims which is in the form of an aqueous solution or an aqueous-alcoholic solution.

13. A composition according to any one of the preceeding claims which has a pH of 5 to 8.

14. A composition according to any one of the preceeding claims which contains a cationic, nonionic, anionic or amphoteric detergent or a mixture thereof and is in the form of a shampoo.

15. A composition according to claim 14 which contains 3 to 50% by weight of detergent.

16. A composition according to any one of claims 15 to 13 which contains a cosmetic resin and is in the form of a wave-setting lotion or a lacquer.

17. A composition according to any one of claims 1 to 13 which contains a hair dyeing agent and is in the form of a hair dyeing composition.

18. A composition according to any one to 10 in which the copolymer is present at a concentration of 0.1 to 10% by weight and is in a form suitable for application to the skin.

19. A composition according to claim 18 which is in the form of a cream, a milk, an emulsion, a gel or an aqueous or aqueous-alcoholic solution.

20. A composition according to any one of the preceeding claims which contains at least one of a perfume, dye, preservative, thickener, stabiliser, softener, sequestering agent, emulsifier, anti-sunburn agent, cicatrising agent, moisturising agent, pigment, filler or anti-inflammatory agent.

21. A composition according to any one of the preceeding claims in which the copolymer is one substantially as described in any one of Examples 1 to 7.

22. A composition according to claim 1 substantially as described in any one of Examples A to D.

Printed in the United Kingdom for Her Majesty's Stationery Office, Dd 8818935, 1985, 4235.
Published at The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.